Applied Energy xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Use of reactive distillation in biodiesel production: A simulation-based comparison of energy requirements and profitability indicators

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HIGHLIGHTS

- Simulation of two reactive distillation processes for biodiesel production is showcased.
- Column duty optimization and heat integration is performed for both processes.
- Economic analysis was performed using different profitability indicators.
- Heterogeneous-catalyzed process is more advantageous over alkali-catalyzed process.

ARTICLE INFO

Article history:
Received 9 August 2015
Received in revised form 8 December 2015
Accepted 14 December 2015
Available online xxxx

Keywords:
Biodiesel
Reactive distillation
Process simulation
Column grand composite curves
Profitability analysis

ABSTRACT

The advent of biodiesel, as a viable alternative to replace crude-based diesel as transport fuel, has prompted growing interest worldwide due to the need for low-emission fuels. In this work, two reactive distillation processes using soybean oil as main feedstock along with the corresponding downstream separation units are simulated: the first process involves a homogeneous alkali catalyst; whereas the second involves a heterogeneous catalyst. Both processes yield a high purity biodiesel product. In the present work, ASPEN Plus v8.4 is used as the process simulation tool. The energy requirements of both processes were evaluated based on the optimization of the distillation column duties and performing heat integration on the process streams. The optimization of the column duties was performed by analyzing the Column Grand Composite Curves (CGCC). The process streams were heat integrated, and a Heat Exchanger Network (HEN) was designed to minimize utility consumption. Both processes were compared using profitability indicators such as Return-On-Investment (ROI), payback period and unit production cost. The results show that the heterogeneous-catalyzed process is more profitable than the alkali-catalyzed process for biodiesel production. The ROI, payback period and unit production cost were 486%, 0.2 years and $0.712 per kg of biodiesel respectively. For the analysis, an annual production capacity of 35.4 kilotonnes/year of biodiesel production was assumed.

1. Introduction

In recent years, biofuels have emerged as a promising renewable energy source. Among the many biofuels, biodiesel has shown great potential as a viable and popular alternative to standard crude-based diesel fuel. There are numerous advantages for the use of biodiesel: (1) synthesis from domestic renewable sources (e.g., vegetable oil), (2) net carbon dioxide emissions reduction of 78% (on a lifecycle basis) compared to crude-based diesel, (3) environmentally friendly given its biodegradable and non-toxic nature, and (4) significantly improves engine exhaust emissions [1]. Biodiesel or mono-alkyl ester of long chain fatty acids can be obtained from triacylglycerols (mainly present in vegetable oil and fat) either by transesterification or esterification processes [2,3]. In the former, the transesterification reaction occurs between triacylglycerols and a low molecular weight alcohol (e.g., methanol) to produce a complex mixture of Fatty Acid Methyl Esters (FAME which is essentially biodiesel) and glycerol. In the esterification or hydroesterification process, triacylglycerols are hydrolyzed to free fatty acids, and then esterified with an alcohol (e.g., methanol) to produce biodiesel and water.

The transesterification reaction requires a catalyst that can either be in the form of a homogeneous alkali, a homogeneous acid, or a heterogeneous alkali. In cases where the reaction is carried out in supercritical conditions, there is no need for a catalyst [4]. For supercritical conditions, the transesterification takes place using alcohol at supercritical state (at a temperature higher than its

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http://dx.doi.org/10.1016/j.apenergy.2015.12.054
0306-2619/

critical temperature). This eliminates the need for a catalyst. For low molecular weight alcohol such as methanol, high temperatures (up to 350 °C) and large alcohol-to-oil ratio (42:1) are required for the reaction to achieve high conversion levels [4]. Many process simulation approaches have been used to model biodiesel production through transesterification reaction. These approaches have included the use of different types of catalysts (i.e., alkali, acid or heterogeneous alkali), feedstock (pure vegetable oil or waste cooking oil), and reaction conditions (normal or supercritical) [1,4–13]. A standard simulation study comprises the simulation of the transesterification reactor, followed by the downstream product purification steps. One of the major developments in the simulation of biodiesel processes consists of modeling the transesterification reaction using a reactive distillation column. This is because the transesterification between the triacylglycerols and alcohol is an equilibrium limited reaction. Thus, the excess alcohol is added to favor the reaction conversion towards biodiesel. This, in turn, requires an expensive set-up to separate the large quantities of unreacted alcohol from the biodiesel product. Integrating the transesterification process and separating the reaction products within the same unit, such as reactive distillation, overcomes the limitations of equilibrium-based reactions. This allows for higher biodiesel yields, by shifting the chemical equilibrium to the product, compared to the conventional processes (reactor–separator set-up). Apart from this, other advantages of reactive distillation include reductions in the number of process units and savings in the overall costs (no longer need of a reactor). Since the esterification reaction is also equilibrium-based, reactive distillation is used to simulate the esterification process of biodiesel production as well.

Several studies have focused on the use of reactive distillation to model the esterification reaction for biodiesel production [2,3,14–18]. In all of these studies, it was found that sufficiently high reaction conversion and product purity were obtained by using reactive distillation. The esterification reaction for biodiesel production primarily involves the usage of heterogeneous acid catalysts. For the simulation of biodiesel production using reactive distillation enabling transesterification reaction, most of the previous works include homogeneous alkali catalyst [19–21]; whereas very limited work is available on heterogeneous catalyst [22]. Mueanmas et al. [19] studied the feasibility of using reactive distillation for the production of biodiesel enabling transesterification reaction using Aspen Plus simulation software. They found optimum conditions for the design and operation of reactive distillation column in terms of molar ratio of alcohol to oil, reboiler temperature, residence time, alcohol to feed location and reflux ratio. Prasertsit et al. [20] studied a simple laboratory scale reactive distillation set up of a packed column for the transesterification of palm oil with methanol. They experimentally determined the optimal operating conditions for the reactive distillation operation. Their results were closely similar to the one obtained by Mueanmas et al. [19]. Simasatitkul et al. [21] simulated and analyzed the optimal conditions required for the design of reactive distillation column (in terms of molar ratio of alcohol to oil, reboiler temperature, alcohol to feed location and reflux ratio) enabling transesterification reaction between soybean oil and methanol for the production of biodiesel using alkali catalyst. Gaurav et al. [22] simulated the transesterification of triacylglycerols to FAME by using a heterogeneous catalyst. They investigated and compared the utility requirements and capital costs between the catalytic reactive distillation and conventional (reactor–separator set-up) process for biodiesel production. They concluded that the catalytic reactive distillation process is more competitive alternative for biodiesel production in terms of capital and utility costs. They also concluded that the cost of oil feedstock is the most significant aspect in the total operating costs of both the biodiesel production processes. Boon-anuwat et al. [23] designed and simulated four different processes for biodiesel production using transesterification reaction between soybean oil and methanol in Aspen Plus simulation package. Four different processes simulated were based on homogeneous alkali catalyst and heterogeneous acid catalyst for both conventional (reactor–separator set-up) and reactive distillation processes. They concluded that the reactive distillation process using heterogeneous catalyst was the best among the considered processes as it had reduced energy consumption and reduced number of units in its process design. Similar to the esterification process, it is known from the Refs. [19–23], that the reactive distillation based biodiesel production processes is more superior and advantageous compared to the conventional biodiesel processes. From the review of the literatures [19–23] for the simulation of reactive distillation based biodiesel production processes using transesterification reaction, we have noticed certain research gaps in the current trend (reactive distillation based biodiesel production processes) which need to be addressed. These gaps are identified as follows.

1. Most of the studies on the reactive distillation process for biodiesel production have focused on the esterification reaction for biodiesel production [2,3,14–18]. Despite the transesterification process being the most important biodiesel production process, only limited studies [19–23] exists for the use of reactive distillation enabling transesterification reaction in the biodiesel production process.
2. Among the reactive distillation enabled transesterification reaction biodiesel production processes, the homogeneous alkali catalyst and heterogeneous catalyst are the well-known processes. To the best of the authors' knowledge, except the work of Boon-anuwat et al. [23], a comprehensive comparison (energy and economic based) between both processes (i.e., homogeneous alkali and heterogeneous catalyst), is currently lacking in the literature. Boon-anuwat et al. [23] provides a comparison between biodiesel production using homogeneous alkali catalyst and heterogeneous catalyst. However, their work does not include cost comparisons between both processes.
3. Although the previous literature work [19–23] does compute the energy requirements and finds out the optimal conditions necessary for the reactive distillation based biodiesel process using transesterification reaction (using homogeneous alkali catalyst or heterogeneous catalyst), there is no work in the literature which systematically carries out optimization approaches to minimize the energy requirements for the reactive distillation based biodiesel process enabling transesterification reaction. The energy reduction approaches for the downstream biodiesel product separation steps have also been overlooked by the previous literature work, as most of it concentrates primarily on the energy aspects and optimum conditions for the main reactive distillation column (reactive distillation based biodiesel process enabling transesterification reaction).

Addressing all of the above mentioned issues/gaps constitutes the motivation of this present work. Therefore, the objective of this work is to find the more suitable reactive distillation process for biodiesel production using a process simulation approach. The transesterification reaction pathway has been chosen for the biodiesel production. In this study, AspenPlus™ by AspenTech has been used as the simulation software. Both (homogeneous alkali and heterogeneous catalyst) processes are compared in terms of energy efficiency, cost effectiveness and profitability to determine the most suitable one. The following assumptions were considered for the simulation purposes: (1) the acceptable final product biodiesel purity must be at least 98% (molar) pure while the

Please cite this article in press as: Poddar T et al. Use of reactive distillation in biodiesel production: A simulation-based comparison of energy requirements and profitability indicators. Appl Energy (2016), http://dx.doi.org/10.1016/j.apenergy.2015.12.054